THE CATALYTIC AMINATION OF ALCOHOLS.

DISSERTATION

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THE CATALYTIC AMINATION OF ALCOHOLS.

Introduction.

The marked lack of definite data on the higher alkyl
amines and the wide field yet open for investigation among
their derivatives make desirable a critical study of the
practicability of their catalytic preparation in a continuous
manner from the corresponding alcohol and ammonia. Sabatier
and Mailhe[1] have shown that a mixture of primary, secondary
and tertiary amines is formed by passing the vapor of an al-
cohol with ammonia over a variety of catalysts at elevated
temperatures. Alumina, titania, zirconia, chromic oxide, the
blue oxide of molybdenum, thoria, and the blue oxide of tung-
sten have been listed as catalysts, the last two mentioned
being commonly regarded as the most efficient. While con-
siderable qualitative data are available, the theoretical and
practical importance of the reaction makes it advisable to
secure more quantitative information than is now at hand. Hence
the present investigation has for its purpose the quantitative
study of the conversion of methyl, ethyl, n-propyl, and n-butyl
alcohols by ammonia into a mixture of the corresponding primary,

1. Sabatier: La Catalyse en Chimie Organique; Paris, 1920,
            pp. 287-291.
        Sabatier and Mailhe: Compt. rend. 143, 1200 (1901);
            148, 898 (1909); 150, 823 (1910); 153, 160(1911

secondary, and tertiary amines, - using various catalytic oxides at temperatures up to 500° C.

Apparatus.

The furnace used was the same as described by Kramer and Reid[1] and the methods of operation similar. The anhydrous alcohol, accurately measured from a regulated dropper and calibrated dropping tip, was led through a vertical tube to the bottom of a 150 c.c. distilling bulb, immersed in an oil bath kept at 250°- 300°, which served as a vaporizing and mixing chamber and a preheater. Ammonia, drawn from a cylinder, passed through a calibrated flowmeter and entered the mixing chamber through a side tube sealed into the vertical alcohol inlet tube. The reactants, passing from the side arm of the vaporization bulb, were led through an extension of the catalytic tube, where they were brought to the proper temperature by a preheating electric coil, and thence over the catalyst in the reaction tube proper, a pyrex tube (1.5-2 cm. x 45 cm.) uniformly heated in a horizontal electric furnace automatically regulated to within $\pm 1°$ as read on a thermocouple laid along the catalyst tube. The resultants of the reaction passed from the catalytic tube through a condenser into a collection bottle.
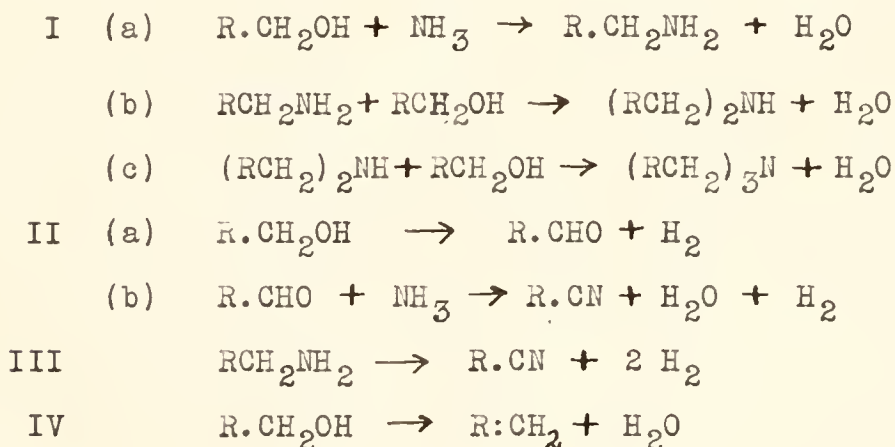
1. Journal Amer. Chem. Soc. __43__, 880 (1921).

A three-way stop-cock interposed permitted samples of the condensate to be taken without disconnecting the main receiver.

Reaction Products.

The condensate, in the case of n-butyl alcohol, consists of a lower, or water layer, and an upper, or main product layer. Only one layer was observed with the three lower alcohols. An alcohol and ammonia lead to primary, secondary, and tertiary amines, aldehyde, nitrile, and water with un-reacting alcohol and ammonia in the condensate and to hydro-gen and ethylene hydrocarbon as permanent gases in accordance with the following reactions:

$$\text{I} \quad \text{(a)} \quad R.CH_2OH + NH_3 \rightarrow R.CH_2NH_2 + H_2O$$

$$\text{(b)} \quad RCH_2NH_2 + RCH_2OH \rightarrow (RCH_2)_2NH + H_2O$$

$$\text{(c)} \quad (RCH_2)_2NH + RCH_2OH \rightarrow (RCH_2)_3N + H_2O$$

$$\text{II} \quad \text{(a)} \quad R.CH_2OH \rightarrow R.CHO + H_2$$

$$\text{(b)} \quad R.CHO + NH_3 \rightarrow R.CN + H_2O + H_2$$

$$\text{III} \quad RCH_2NH_2 \rightarrow R.CN + 2 H_2$$

$$\text{IV} \quad R.CH_2OH \rightarrow R:CH_2 + H_2O$$

Analysis.

After an extensive study of all the methods [1] that have been proposed for such mixtures we decided on the following plan, which is essentially that proposed by Weber and Wilson[2], though we did not come across their work until after our own was done. The method was tested out on known mixtures and the corrections thus found applied to the unknowns.

The reaction products were run for the desired time into standard sulphuric acid and titrated back with methyl red as indicator to determine total basic nitrogen. The solution was divided into aliquots, in one of which the total amine nitrogen was found by the method of Francois[3] based on the selective precipitation of ammonia in presence of amines in a sodium hydroxide - carbonate solution by yellow mercuric oxide. The difference of these two represents the ammonia. In a

1. Heintz: Annalen, 127, 43 (1863).
    Höfmann : Berichte, 3, 776(1870).
    Hinsberg: Berichte, 23, 2962(1890); 33, 3526-9 (1900).
    Hinsberg and Kessler: Berichte, 38, 906(1905).
    Sudborough: Proc. Roy. Soc., 20, 165 (1904); J. Chem.
              Soc., 95, 447 (1909).

    Bertheanme: Compt. rend., 150, 1251-3 (1910);
                            151, 146-9 (1911).

2. Jour. Biol. Chem., 35, 385 (1918).

3. J. pharm. Chimie, (6) 25, 517 (1907).
    Compt. rend., 144, 567-9 (1907); 857-9 (1907).

second aliquot ammonia and primary amine are determined to-
gether by the method of van Slyke[1] for the estimation of the
amine group, the decomposition being effected at 90° C. Tests
with pure ammonium chloride and the hydrochloride of butyl
amine prepared by the reduction of nitrobutane gave results
2 % high, agreeing with van Slyke's observations on other
amino compounds. Subtracting the previously determined am-
monia from the van Slyke value gives the primary amine.

To estimate tertiary amine a third aliquot is placed in
a 200 c.c. flask and sufficient sodium nitrite added to make
a 25 % solution. This is heated for an hour under reflux on
a water bath, acetic acid being added from time to time to
maintain acidity. A trap containing dilute sulphuric acid
was connected with the top of the condenser to guard against
loss of amine. After cooling the solution is transferred to
a Kjeldahl still, nitrogen oxides blown off and strong alkali
added, after which the tertiary amine is distilled into stan-
dard sulphuric acid and back titrated with methyl red as indi-
cator. The secondary amine is estimated by difference from
the above determinations.

The estimation of nitrile is effected by hydrolysis of
an aliquot of the sample with 40 % (by volume) sulphuric acid
in a pressure bottle at 100° for 1 hour. The product is
diluted and steam distilled into 0.1 N. alkali and back titrated

1. Berchite, _43_, 3170 (1910).

with phenolphthalein as indicator to determine the acid
resulting from the hydrolysis of the nitrile.

Inasmuch as the amines are estimated through their nitro-
gen value, a complete analysis sample for primary, secondary,
and tertiary amines is necessary for the true determination
of the percentage of alcohol aminated, since primary, second-
ary, and tertiary amines are equivalent as regards the nitrogen
value. As a result, the ratio of total amine nitrogen, as
determined, to the alcohol nitrogen equivalent gives a low
value for total percentage amination of the alcohol, the lower,
the higher the percentages of secondary and tertiary amines in
the sample. Consequently, two values for percentage amination
will be met with in the following tables of experimental results:
the one, used when only total amine was estimated, termed simply
"% amines" which counts all the amines present as primary, that
is, the number of molecules of amine from 100 of alcohol; the
other, "% alcohol aminated", used when complete analyses were
made for primary, secondary, and tertiary amines. This value
is found by adding twice the secondary and three times the
tertiary amines present to the primary, and represents the ac-
tual amount of alcohol converted into amines. On the average
this figure is 1.69 times the "percent of amines", varying,of
course, with the ratio of secondary and tertiary to primary
but remaining quite constant for butyl alcohol.   In cases
where complete analyses were not made, the percent of

alcohol aminated can be approximated by multiplying the "% amines" by this factor. For closer approximations the variation of this factor with temperature should be considered. For the preliminary comparison of catalysts it is sufficient to consider the total amines formed as set down under "% amines".

Analysis of the gases was effected by collection of a timed sample in a Hempel burette over dilute sulphuric acid, adsorption of the ethylene hydrocarbon by fuming sulphuric acid, and determination of the residual hydrogen by explosion - in later runs by difference. The gas left after shaking with fuming sulphuric acid was found to contain practically nothing but hydrogen.

As an alcohol may pass to a nitrile by a two step process- aldehyde being the intermediate stage - with the liberation of two atoms of hydrogen at each step, the aldehyde in the con- densate can be calculated from a knowledge of the nitrile and of hydrogen gas values.

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Experimental.

Thoria Catalyst. Figure I.

In view of the efficiency of thoria as a dehydrating catalyst, this was the first catalytic substance employed. Catalyst A was prepared by pouring over enough shredded asbestos to fill the catalytic tube an almost saturated solution of thorium nitrate corresponding to 25 g. thoria, and evaporating to dryness in a vacuum desiccator over sulphuric acid. The resulting hard mass was shredded into small fragments, packed in the catalytic tube, and heated to 270°- 300° in the furnace whereby the nitrate was converted to the oxide. After complete conversion, the catalyst was thoroughly scrubbed out with moist air at 400°C.

This catalyst was employed for the amination of butyl alcohol as shown in Table I. Some of the runs were at temperatures differing slightly from those given, but, as the temperature coefficient is not great, they have been grouped. The rate is time in hours required for the passage of one mol of the alcohol over the catalyst. For the first run only were the amines determined separately.

TABLE I.

Catalyst A. Figure I.

Part 1

Butyl Alcohol and Ammonia over Thoria - Asbestos.

	Run I
NH_3/BuOH	1.5
Rate	6
Hrs. previous use of catalyst	0

Temp.	Amines formed			% Alcohol	% Amines
	prim.	second.	tert.	aminated	formed
360°	___	___	___	___	___
370°	15.9	7.8	16.5	40.2	25.3
380°	13.1	14.8	20.4	48.3	27.3
390°	14.6	17.8	13.5	46.0	28.0
400°	___	___	___	___	___
410°	8.9	19.4	12.0	40.3	22.6
420°	___	___	___	___	___
430°	8.6	4.5	13.8	26.9	15.4

TABLE I.

Catalyst A.   Figure I.
Part 2

Butyl Alcohol and Ammonia over Thoria - Asbestos.

Run	I	II	III	IV	V	VI
NH$_3$/BuOH	1.5	2.4	1.6	1.15	1.15	1.5
Rate	6	9	3.1	8.9	6	6
Hrs. previous use of catalyst	0	10	15	20	30	40
Temp.			Percent	Amines	formed	
360°	___	16.7	7.0	10.2	4.0	___
370°	25.3	___	7.6	12.7	3.6	___
380°	27.3	19.3	___	___	___	___
390°	28.0	21.3	8.1	14.6	5.1	8.9
400°	___	___	7.2	___	5.9	___
410°	22.6	___	7.2	17.2	___	___
420°	___	16.8	___	12.9	6.3	___
430°	15.4	16.3	7.4	___	___	___

The optimum temperature is 360°-390° for a fresh catalyst but rises to 420° or higher with prolonged use, the deterioration of the catalyst being more rapid during the first part of its life period. After having become coated with a carbonaceous deposit, the catalyst may be regenerated by treatment for several hours at 380°-400° with moist oxides of nitrogen, followed by moist air, but does not recover its original activity, as is shown by Run VI above. The regenerated catalyst is pure white but its surface is distinctly different - appearing grainy rather than powdery as it did originally.

Catalyst B was made in a similar manner with pumice as carrier. A concentrated solution of thorium nitrate equivalent to 25 g. thoria was poured over the amount of broken pumice required to fill the reaction tube and treated as above.

This catalyst was tested with butyl alcohol at the rate of 1 mol. in 5.8 hours with 1.3 equivalents of ammonia, with the following results:

TABLE II.

Temp.	326°	342°	355°	369°	385°	396°
% Amines	1.64	3.65	4.18	6.65	8.55	10.2

The catalyst became darkened by a slight deposit but still appeared to be in good physical condition with a characteristic smooth surface.

Gas Evolution.

Thoria has been rated by Sabatier[1] as a dehydration
catalyst exclusively, but Kramer and Reid[2] found only 2.7 %
of butylene to 32.7 % of butyric aldehyde produced by their
thoria catalyst at 380°, from which it appears that different
preparations of thoria give widely different results. When
ammonia is present the aldehyde formed is largely, but not
completely, converted into nitrile with the evolution of a
second molecule of hydrogen. Actually the furnace product
gave, on distillation, a small fraction which smelled of al-
dehyde and gave the aldehyde test with fuchsine solution.

A run was made using the thoria-asbestos catalyst A
with butyl alcohol vapor, 1 mole in 5.6 hours, and a slight
excess of ammonia, the gas being collected and analyzed. If
all of the alcohol had been converted to aldehyde 64.3 c.c.
of hydrogen should have been formed per minute, if into
nitrile, 128.6 c.c. and if into butylene, 64.3 c.c. of C_4H_8 .
The results are given in Table III, the volume given being
cubic centimeters obtained per minute reduced to 0° and 760 mm.

1.   La Catalyse,   Paris, 1920, p. 251.
2.   Journal Amer. Chem. Soc. 43, 884 (1921).

TABLE III.

Gas evolved from butyl Alcohol and Ammonia.

Temp.	Total Gas	C_4H_8	H_2	% Alcohol converted into	
				C_4H_8	Nitrile
360°	10.3	1.17	8.97	1.82	6.98
374°	16.02	2.26	13.34	3.52	10.38
390°	29.87	4.02	23.90	6.25	18.60
405°	33.21	4.17	29.00	6.48	22.59
420°	57.28	8.04	49.25	12.5	38.3

The figures under "nitrile" were calculated on the assumption that all of the aldehyde formed had been converted into nitrile, that is by dividing the percentage of hydrogen by 2 which over-estimates the nitrile since some of the aldehyde remained as such. In a similar run using 1.45 mol. of ammonia to 1 of alcohol at the same rate, the nitrile was found to be 11.05 % and 22.3 % at 380° and 410° whereas calculated as above it would have been 12.8 % and 29.5 %. Calculating the aldehyde from the hydrogen remaining after subtracting that corresponding to the nitrile we have 3.5 % and 14.4 % of aldehyde remaining as such. Our thoria-asbestos was a poor catalyst for dehydrating butyl alcohol but excellent for producing aldehyde and nitrile by dehydrogenation. Above 400° a large proportion of the alcohol is used up in side reactions.

Tungstic Oxide Catalysts, Figure II.

Catalyst C. A tungstic acid hydrate gel[1] was made by the gradual addition of 6.38 N. nitric acid to a 12 % solution of sodium tungstate in a large crystallizing dish -- slowly until the first formed precipitate redissolves, then rapidly with vigorous stirring until the colorless solution takes on a clear yellow green color, the total acid required being 2.5 to 3.0 times the sodium tungstate equivalent. The gel after having set is thoroughly washed, and slowly dried at gradually increasing temperatures, and finally reduced at 300° with hydrogen to the blue oxide. Seventy-eight grams of the reduced blue oxide gel were employed as the catalyst with which two runs were made.

Catalyst D. Unhydrated tungstic acid prepared by precipitation from a hot solution containing 25 g. sodium tungstate, was thoroughly washed and in the form of a thin paste was distributed over small fragments of pumice. This material was then slowly dried and reduced at 275°-350° with ethyl alcohol vapor carried over it by air.

Catalyst E. Tungstic acid, prepared by precipitation of a hot solution, containing 25 g. of sodium tungstate, with hot concentrated hydrochloric acid, after being thoroughly washed,

1. Method worked out in this laboratory by Dr. C. H. Milligan to whom we are indebted for 32 g. of this gel.

was dissolved in a water solution of ethyl amine. Pumice broken into small fragments was then impregnated by slow evaporation of this solution. The pumice fragments, evenly coated with a white deposit of the salt, were packed in the catalytic tube and heated to 300° in a slow current of air. The ethyl amine tungstate was thus decomposed with the formation of blue oxide of tungsten and some tungsten trioxide which latter was reduced to the blue oxide with an air-ethyl alcohol vapor mixture at 350°. The resulting catalyst was notable for its adherent qualities and even distribution of the blue oxide.

Catalyst F. This catalyst was prepared by suspending 40 g. of commercial blue oxide of tungsten powder on pumice.

The efficiency of these catalysts in amination was found to be surprisingly low, the most active being that from ethyl amine tungstate. Though each of the blue oxide of tungsten catalysts were subjected to 10 to 12 working hours of catalysis, their physical properties seemed entirely unimpaired - no carbonization being observed. The results with these catalysts are given in Table IV.

TABLE IV.

Figure 2 for C and D

Alcohol and Ammonia 1:1.5 over Oxide of Tungsten.

Catalyst	C	C′	D	E [1]	F
Alcohol	Butyl	Butyl	Butyl	Butyl	Ethyl
Rate	8	5.7	5.7	5.2	5.8
Temp.		Percent	Amines	Formed	
305°	____	____	2.78	0.36	2.04
320°	____	____	3.43	____	____
335°	1.68	1.01	____	____	____
340°	____	____	2.98	____	5.05
350°	1.73	1.21	____	____	____
365°	2.98	1.55	2.10	*6.22	6.77
380°	1.98	1.32	____	____	____
400°	1.12	0.84	0.76	____	7.73
420°	____	____	____	____	7.04
460°	____	____	____	____	5.16

1. Analysis made on a two hour sample at 305° and a two and a half hour sample at 365°.

The gases evolved were collected and analysed with
catalyst E at 365⁰ as indicated by the * with the following
results:

Temp.	Total gas	C_4H_8	H_2	% C_4H_8	% Nitrile
365⁰	23.3	19.4	3.9	26.8	2.69
365⁰	20.8	17.8	3.0	25.3	2.18

from which it appears that the blue oxide of tungsten is a
decided dehydration catalyst - agreeing well with the findings
of Sabatier and Mailhe[1].

1. Ann. chim, phys., (8) 20, 328(1910).

Miscellaneous Catalysts. Figure II.

Catalyst G consisted of 20 g. of alumina precipitated on pumice from sodium aluminate by sulphuric acid. It became heavily carbonized in a single run with butyl alcohol and ammonia.

Catalyst H was prepared similarly to B using 25 g. zirconium nitrate on pumice. It carbonized badly in a single run.

Catalyst I was 30 g. of a laboratory stock sample of silica gel which had been kept for about a year in contact with the air. After a run with butyl alcohol it was considerably discolored, amber to dark brown, but showed no surface deposits.

Catalyst J[1] was 30 g. of silica gel impregnated with a small percentage of thoria. It showed only slight discoloration in one run.

Catalyst K[2] was 30 g. of silica gel impregnated with nickel oxide which was reduced by the alcohol. It proved to be an active dehydrogenation catalyst producing much nitrile. It discolored about as I.

The performances of these catalysts can be seen in the following table which gives the percent amines formed at various temperatures.

1. For catalysts J and K we are indebted to Mr. E. H. Barclay of this Laboratory.

TABLE V.

Figure 2.

Butyl Alcohol and Ammonia, 1:1.5

Catalyst	G	H	I	J	K
Rate	5.6	5.75	5.58	5.75	5.8

Temp.		Percent	Amines	Formed	
305°	2.57	8.6	0.87	———	———
320°	3.32	10.3	0.89	———	5.68
330°	———	———	———	13.4	8.05
340°	4.55	14.0	1.58	15.0	———
350°	———	———	———	———	*9.63
360°	6.00	15.0	———	16.4	———
370°	———	———	2.82	———	———
380°	6.55	13.5	———	15.4	8.10
390°	———	———	4.60	11.1	———
405°	5.38	8.15	———	4.6	*6.03

At 350° and at 405° with catalyst K as indicated by *
analysis showed 24.7 % and 40.1 % of nitrile on the alcohol
used.

Special Silica Gel.

Figures 3 and 4

While as shown above commercial silica gel prepared according to Patrick's method[1] is only a fair catalyst, yet if precautions are taken in its preparation, both in the use of pure chemicals and in thorough washing, it shows a far greater activity in amination[2]. Such silica gel appears to be superior to all other catalysts so far tried, in availability, length of life, high efficiency and low dehydrogenation power.

Our gel was prepared[4] by adding, with vigorous stirring, a sodium silicate solution (4.5 % Na_2O) to an equal volume of 10 % pure hydrochloric acid. After the gel sets, it is broken into large fragments which are placed in a tray having a bottom of wire or cloth netting suspended in running water for several days. The gel is dried at temperatures rising by stages to 160°- 180° before being placed in the catalyst tube.

For charging the reaction tube 30 g. of the gel in fragments 0.5 to 0.7 cm. were required. After running for 25 hours with butyl alcohol and ammonia there was no diminution in the activity of this catalyst. All of the runs in the following table were made with the same sample[3] of catalyst, the runs are numbered in the order in which they were made.

1. U. S. patent 1,297,724 March 1919.
2. In esterification Dr. Milligan of this Laboratory found the commercial gel as active as the specially prepared.
3. Kindness of Mr. E. H. Barclay of this Laboratory.
4. Method in use in this laboratory.

TABLE VI.

Figure 3.

Alcohols with Ammonia 1:1.5   Special Silica Gel.

Run	3	2	4	5	1
Alcohol	Methyl	Ethyl	Ethyl	Propyl	Butyl
Rate	5.9	5.6	5.6	6.2	5.5
Temp.		Percent	Amines	Formed	
300°	___	___	___	___	3.7
320°	5.4	5.1	5.6	14.6	5.4
340°	8.4	9.5	8.9	19.8	6.5
360°	12.4	12.75	12.1	24.1	8.1
380°	17.0	18.5	19.9	26.4	11.7
400°	23.3	25.6	25.6	29.6	18.3
420°	31.0	31.1	30.8	32.4	20.7
430°	___	___	___	___	20.4

Propyl alcohol appears to be the most readily aminated. About 400°- 420° is the best temperature.

The run of butyl alcohol was continued for 185 minutes using 0.56 mole of the alcohol. The lower layer of the product weighed 8.59 g. and contained 0.0034 moles of amines while the top layer weighed 24.78 g. with 0.11 moles of amines

or 20.3 %. A new run was made with the same gel and samples taken at intervals with the following results: after 1 h. 22.8 %, after 6 h. 23.2 %. After standing cold over night it was started again and gave: after 1 h. 22.4 %, after 3 h. 20.7 % and after 6 h. 22.9 % amination.

The gases evolved were studied and found as follows:

TABLE VII.

Temp.	Alcohol	Gas per min.	C_nH_{2n} c.c.	H_2 c.c.	C_nH_{2n} %	H_2 %	
400°	Ethyl	7.77	3.28	4.48	4.72	3.22	
415°	Butyl	8.90	6.75	2.15	10.90	1.75	(fresh gel)
415°	Butyl	12.85	7.85	5.00	12.80	4.06	(long used gel)

From these figures it appears that silica gel dehydrates moderately well but dehydrogenates very slightly as compared to thoria, which is a great advantage in this reaction.

Complete runs and analyses on methyl, ethyl, n-propyl and n-butyl alcohols using fresh samples of gel in each case as catalyst gave the results of Table VIII.

TABLE VIII.

Figure 4

Silica Gel Catalysts.

Experimental Conditions	Cat. Temp.	Alcohol Aminated RNH %	R₂NH %	R₃N %	% Amines (A)	% Total Amination (B)	Ratio B/A
MeOH:NH₃	328°				4.90		
	360°				9.05		
= 1:1.5	395°				16.12		
at	423°	5.91	35.30	6.48	25.72	47.69	1.85
1 Mole in	447°				29.80		
5.5 hrs.	481°	14.35	35.80	5.67	34.14	55.82	1.63
	510°				32.83		
EtOH:NH₃	354°				4.93		
	395°				10.60		
= 1:1.5	415°	4.31	14.74	11.52	15.52	30.57	1.97
at	436°				19.20		
	456°	7.80	19.34	12.24	21.55	39.38	1.82
1 Mole in	477°				22.16		
5.8 hrs.	500°				17.34		
	520°				14.24		
PrOH:NH₃	300°				8.02		
	331°				12.70		
= 1:1.5	359°	7.62	20.66	2.28	18.71	30.56	1.63
at	388°				27.85		
	420°	19.50	21.60	7.68	32.86	48.78	1.49
1 Mole in	448°	15.08	6.02	4.29	19.52	25.39	1.39
6.2 hrs.	468°				9.02		
	490°				3.06		
BuOH:NH₃	381°	0.45	19.12	1.59	10.54	21.16	2.05
= 1:1.5	407°	7.40	14.22	2.43	15.32	24.05	1.57
at	430°	10.90	10.72	3.42	17.40	25.04	1.44
1 Mole in	472°	8.37	5.86	4.35	12.75	18.48	1.45
6 hrs.							

A different gel preparation showed with butyl alcohol a
similar maximum yield but a sharper break in the temperature-
yield curve, under similar experimental conditions of molal
ratio of reactants of 1:1.5 and flow rate of a mole of alcohol
per six hours, as Table IX indicates.

TABLE IX.

System BuOH-NH_3

Catalyst Temp.	320^0	354^0	381^0	396^0	420^0	452^0	472^0	493^0
% Amines	3.29	4.77	9.40	10.90	14.44	17.40	6.60	2.86

A silica gel for general commercial catalytic and adsorption pur-
poses prepared for the market by the Davison Chemical Company of
Baltimore was tested on ethyl alcohol for comparison purposes.
Taste revealed the presence of sodium sulphate in this gel but
the quantity present was not determined. Thirty-five grams of
the gel in fragments of about 0.3 cm. diameter were used as a
catalyst charge. The results obtained with ethyl alcohol and
ammonia (Molal ratio 1:1.5 at a flow rate of one mole EtOH per
5.6 hrs.) are given in Table X, whereby it is seen that its
efficiency falls far short of that of the active silica gel
prepared in the laboratory.

TABLE X.

Catalyst Temp.	354	375	402	426	454	481
% Amines	5.28	6.80	9.47	10.21	9.44	9.54

Conclusions.

The results of this investigation reveal the fact that silica gel in the proper physical state is an amination catalyst comparable with freshly prepared thoria in percentage conversion of alcohol, and much superior to thoria as well as alumina and zirconia in length of catalytic life and in freedom from destructive action on the alcohol not aminated. Blue oxide of tungsten is of small value for alkyl amination as compared with silica gel. Impregnated with small amounts of thoria and of nickel oxide, respectively, silica gel falls far short of the unimpregnated gel in maximum percentage amination of alcohols.

Silica gel is preferentially an alcohol dehydrator rather than a dehydrogenator, and in this respect resembles blue tungsten oxide. At the corresponding optimum conversion temperatures of the two catalysts, in the case of butyl alcohol silica gel causes the formation of but half the butylene liberated when blue tungsten oxide is the catalyst, - although the optimum temperature of silica gel is some fifty degrees the higher. Thoria, in contrast, acts preferentially as an alcohol dehydrogenator. At the same temperature, silica gel liberates but 10 % as much hydrogen as thoria, the butylene evolutions of the two catalysts being of the same order.

Whether the dehydration mechanism that produces an amine molecule is one whereby the elements of water are abstracted from an alcohol molecule and an ammonia molecule conjointly, or is rather one whereby the alcohol molecule, itself losing

the full elements of water saturates its nascent double bond with ammonia, is not clear. A test experiment on an ethylene-ammonia mixture over active silica gel at 352°, 400° and 454° revealed no tendency of ammonia to aminate a previously formed double bond.

Thenmost striking fact concerning silica gel as an amination catalyst revealed by this investigation is the comparatively wide variation in the effectiveness of the finished catalyst with seemingly slight variations in the preparation procedure. A single sample of silica gel will give reproducible results, but two samples, prepared individually, will show divergences more or less marked. In general, slow setting of the gel from C. P. reactants used in a definite proportion, long washing, and slow drying are to be emphasized as essential requirements for the production of an active catalytic surface. Variations from such a procedure lead to a gel either crumbly or, if firm, of a porosity unfitted for maximum catalytic activity.
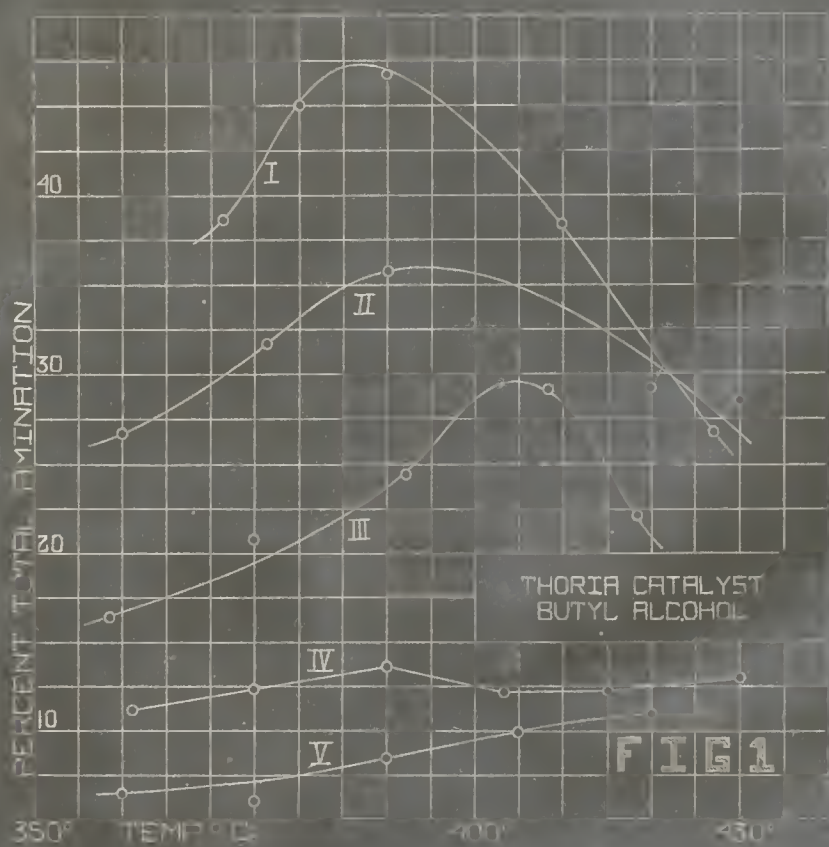
Summary.

The amination of methyl, ethyl, n-propyl, and n-butyl alcohols, by passing their vapors with ammonia over catalysts at 300° - 500°, has been studied quantitatively. The following catalysts, arranged in the order of effectiveness, have been studied: blue oxide of tungsten, commercial silica gel, alumina, silica gel impregnated with nickel oxide, zirconia, silica gel impregnated with thoria, thoria, and special silica gel.
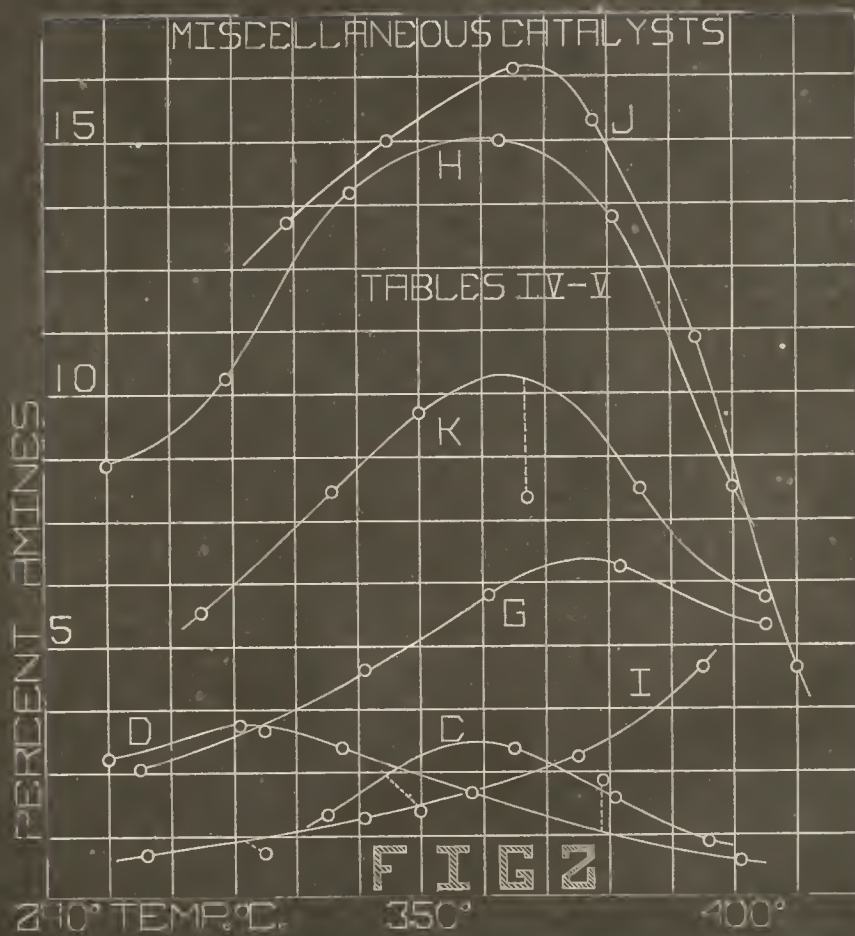
For high activity, long life, and absence of side reactions, the special silica gel has been found to be much the best. The optimum temperatures, percentages of amination, and the ratios of primary, secondary, and tertiary amines formed with the various alcohols are as follows: methyl, 480°, 56 %, 5:12:3; ethyl, 465°, 39.5 %, 2:5:3; n-propyl, 415°, 49 %, 10:11:8; n-butyl, 430°, 25 %, 11:11:3.

PERCENT TOTAL AMINATION

THORIA CATALYST
BUTYL ALCOHOL

FIG 1

MISCELLANEOUS CATALYSTS

TABLES IV-V

FIG 2

PERCENT AMINES

210° TEMP. C.   350°   400°

PR-OH

ET-OH

MC-OH

BU-OH

SINGLE SAMPLE
SILICA GEL CATALYST

FIG 3

PERCENT AMINES

30

20

10

290° TEMP. °C.   350°   400°

FIG 4

SILICA GEL CATALYST

Axis labels: PERCENT TOTAL AMINATION (y-axis), TEMP. °C. (x-axis), 400°, 450°, 500°
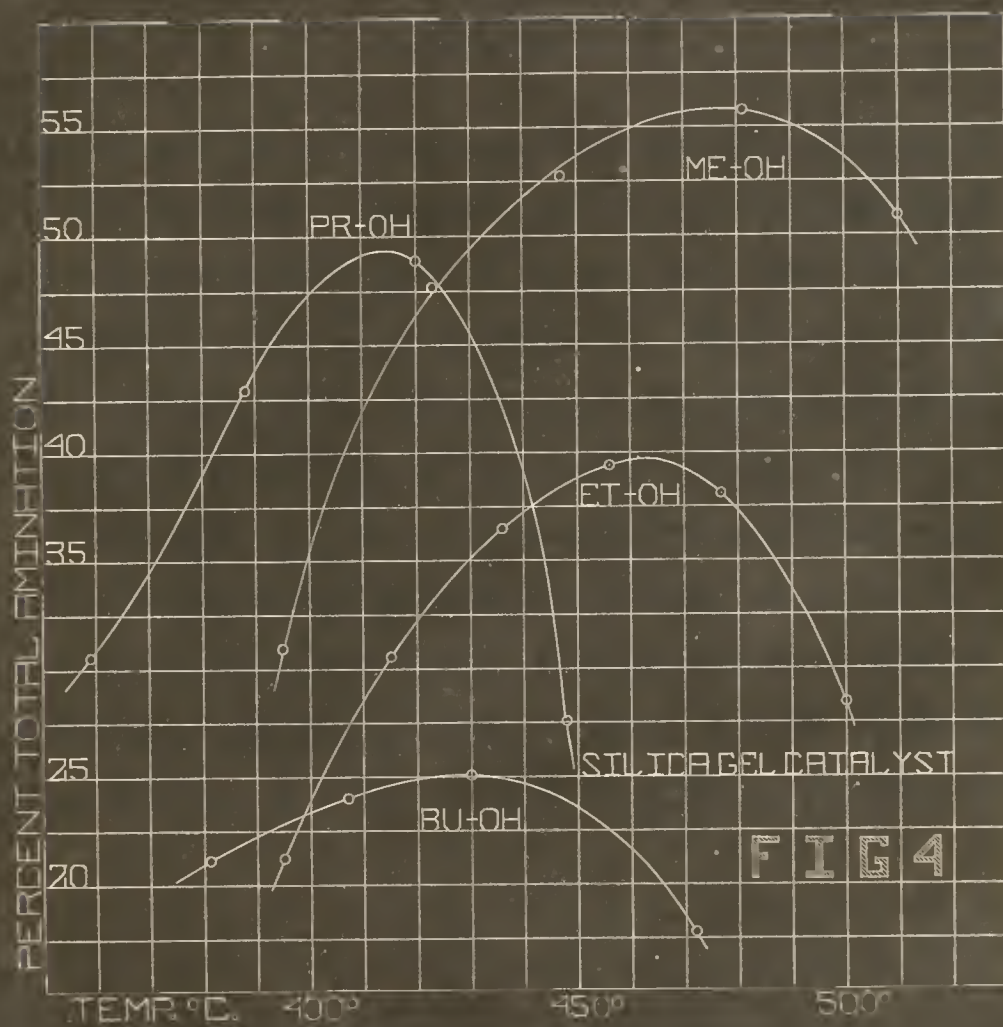
Curve labels: ME-OH, PR-OH, ET-OH, BU-OH
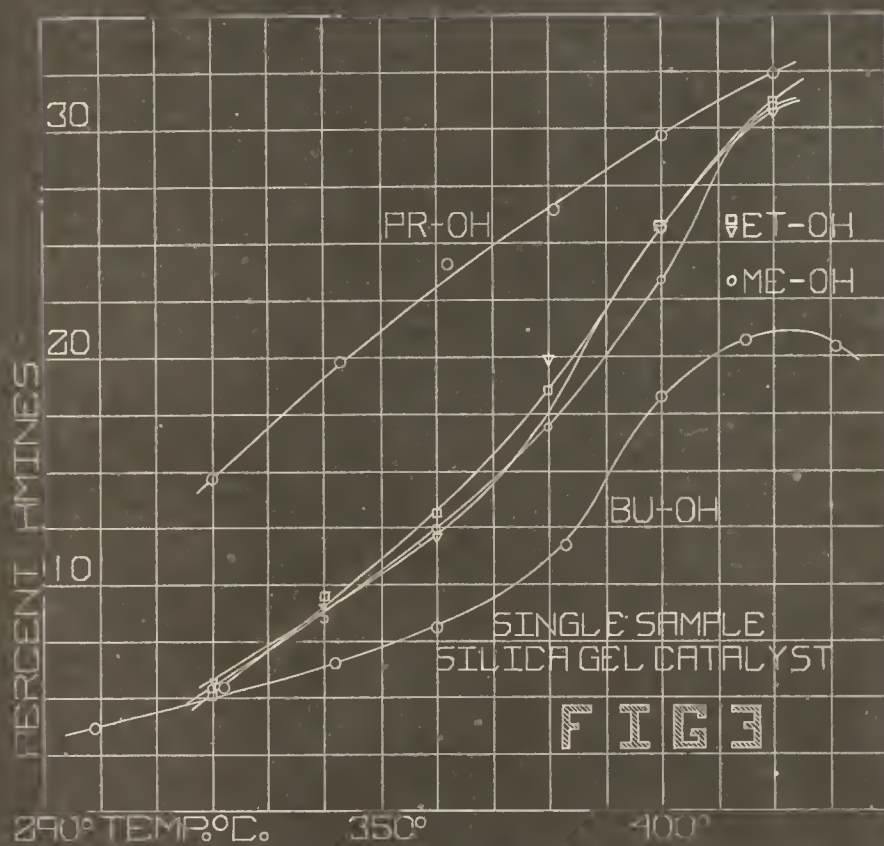
BIOGRAPHY

The author of this dissertation was born at Charleston, S. C., July 17, 1899. He received his early education in the private and public schools of the same city and at the Porter Military Academy of Charleston, from which he was graduated in June 1915. He received the degree of Bachelor of Arts from the College of Charleston in May 1918. In the fall of the same year he entered the Graduate Department of Chemistry of the Johns Hopkins University, majoring in Chemistry with Physical Chemistry and Mathematics as subordinate subjects. He held Hopkins Scholarships for the years 1918-19, 1919-20, 1920-21, and the Du Pont Fellowship for 1921-22.